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CATALYTIC COMBUSTION, A POLLUTION-FREE MEANS OF ENERGY CONVERSION

NATIONAL ENVIRONMENTAL RESEARCH CENTER

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CATALYTIC COMBUSTION, A POLLUTION-FREE MEANS OF ENERGY CONVERSION ?

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by

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ABSTRACT

The report gives results of a study to determine the potential of catalytic combustion for pollution-free domestic heating applications. Fourteen commercially available catalytic heaters were tested. Nine units operated on propane and the other five, on lead-free gasoline. Based on the results with the commercial heaters, a second phase of controlled testing was undertaken. Substrate thickness, catalyst type and concentration, and fuel rate were the parameters examined.

The results show that hydrocarbon (HC) emissions could not be reduced to levels approaching those currently possible with conventional domestic heating units. However, nitrogen oxides (NO_x) emissions were very low from nearly all the heaters. In the controlled testing, substrate thickness and catalyst treatment had small effect on emissions. Fuel rate was the most important parameter, especially in its effect on HC emissions. Also, some of the commercial units produced extremely high levels of carbon monoxide (CO) which the performance of other units and the controlled testing showed to be preventable. Because of the high HC emissions, more research is necessary before catalytic heating can be considered a viable domestic heating alternative.

INTRODUCTION

History

The Control Systems Laboratory (CSL) of EPA's Office of Research and Development is charged with the responsibility for finding and developing techniques by which coal, oil, and natural gas can be burned without producing harmful emissions such as combustible particulates and nitrogen oxides (NO_x). A recent survey [1] has shown that domestic sources account for a significant amount of these emissions, particularly with respect to NO_x. The study further revealed that 95 percent of these units are burning either natural gas or light oil. In-house studies [2,3,4] have shown that, while 30 percent reductions in NO_x can be achieved through careful burner design, no completely effective technique is available. Modifications such as flue gas recirculation, staged combustion, and water injection are too expensive for home units. To overcome these difficulties various new concepts are being considered by the CSL. This document is the final report on an in-house study conducted on one such concept, catalytic combustion. Mention of company and produc. names herein does not constitute endorsement by the U. S. Environmental Protection Agency.

Purpose

The purpose of this program was to determine the potential of catalytic combustion for pollution-free domestic heating applications. Phase I was directed toward the testing of current commercially available catalytic heaters on both relative and absolute bases. Phase II addressed itself to more fundamental considerations; namely, optimization of the surface combustion concept by studying catalyst concentration, pad thickness, catalyst material, and fuel rate. Phase II was necessary because of the wide variation in performance observed during Phase I.

SUMMARY

Fourteen commercially available catalytic heaters were tested in Phase I of this study: nine units operated on propane; and the other five, on lead-free gasoline. Each heater was tested at two fuel rates: (1) the maximum rate at which the heater would operate under the manufacturer's control system,and (2) a common rate of 770 scc/min (4000 Btu/hr). In general the liquid fuel units had higher CO and unburned HC emissions than the propane units. NO_x emissions were very low (less than 20 ppm) from nearly all heaters. An analysis of the results revealed that there was no direct relationship between retail cost and performance; higher priced units do not necessarily provide low emissions (or more heat output). Finally, the fact that some of the units emit extremely high levels of CO (in excess of 1500 ppm) cannot be overlooked due to the actual danger involved.

In an effort to determine the cause of the performance variations in Phase I, Phase II was undertaken. This more fundamental testing considered the effects of substrate thickness, catalyst type and concentration, and fuel rate. Pad thickness had little effect on emissions, but doubling the platinum concentration decreased HC emissions slightly (by 50 to 300 ppm). The addition of 1 percent manganese to the catalyst treatment also slightly decreased HC emissions. The most important parameter encountered during the study was fuel rate, which had an especially strong effect on HC emissions. It appears that part of the difference in performance of the commercial units could be due to incorrect fuel rate design for the pad area.

The Phase II data also confirms that high CO levels are unnecessary and the manufacturers, whose products perform so poorly, should be encouraged to improve them. Under no conditions, however, was it possible to reduce HC emissions to a level approaching that currently possible with conventional domestic heating units (0.05 g per kg of fuel burned). Therefore, more research is necessary to develop catalytic heating as a viable domestic heating alternative.

BACKGROUND

Previous metal gauze catalysts have long been employed in industrial processes such as the manufacture of nitric acid by the partial oxidation of ammonia and the related Andrussow process in which a mixture of ammonia, air, and natural gas is converted to hydrocyanic acid. Application of such catalytically active metals as platinum, palladium, and rhodium on a variety of substrates (for the oxidation of lower order aliphatic hydrocarbons such as propane) in small scale heating uses was suggested by Webster[5] and Weiss[6] in the late 1950's. The global reaction is:

$$C_3H_8 + 5\,O_2 \rightarrow 3\,CO_2 + 4\,H_2O$$

in which the initiation steps for the classical, high temperature combustion are postulated[7] to be:

$$C_3H_8 + OH \leftrightarrow C_3H_7 + H_2O$$

$$C_3H_8 + O \leftrightarrow C_2H_6 + HCHO$$

$$C_3H_8 + H \leftarrow C_3H_7 + H_2$$

In a catalytic heater, this type mechanism is replaced by low temperature (<427°C, <800°F) reaction path utilizing the catalyst present; however, the details of the latter are not well documented. Experiments on the oxidation of hexene and toluene in excess air with platinum screen catalyst[8] have shown that above 370°C (700°F) the oxidation occurs via a mass-transfer-controlled reaction. Satterfield and Cortex[8] have shown that below 370°C (700°F) the effectiveness of the platinum falls off sharply with decreasing temperature. Similar results have been obtained[9] in studies of the oxidation of methane and CO with palladium-impregnated surfaces. They also concluded that, for oxidation of small amounts (ppm) of methane in air, palladium was

far superior to platinum. Recent data obtained by Benvegno[10] shows that platinum is superior for catalytic heating concentrations.

Most commercially available catalytic heaters utilize a catalyst in the form of finely divided particles of catalytically active platinum deposited on a porous, inert, thermally resistant substrate such as asbestos cloth or fibrous silica-alumina. One technique by which the catalyst material can be impregnated on the support material consists of dissolving a thermally reducible compound of the catalytic metal (e.g., H_2PtCl_6) in a solvent, mixing it thoroughly with 10-micron activated alumina, and heating the mixture to reduce the metal and precipitate the metal particles on the alumina. The resultant dry powder is then mixed with water to make a slurry and sprayed onto the support material.[11]

During the operation of the unit, the fuel is conducted to the back of the catalyst pad, allowed to diffuse through the inert backing, and combusted over the face of the unit. Gaseous fuels are fed in via a gas spud having a small central orifice. Liquid units utilize a wick formed of non-combustible fibers such as fiberglass[12] and require that the fuel vaporize between the wick and the back of the catalyst pad. Both types of units require preheating, which is accomplished by lighting raw fuel at the pad surface. When the unit achieves a high enough temperature, the catalytic action begins and the flame goes out.

EXPERIMENTAL APPROACH

Samples Examined

During Phase I of the program, 14 commercially available heaters were procured either through manufacturer solicitation or off-the-shelf purchase. Appendices A and B contain a detailed description of all the units and their respective manufacturers. Nine of the 14 units operate on propane (LPG); the remaining 5 require lead-free ("white") gasoline. All of the units have a heat rating between (1260 kcal/hr and 2016 kcal/hr; 5,000 and 8,000 Btu/hr) based on the heat content of the inlet fuel. These heaters are commonly used by sportsmen in tents, camping trailers, hunting lodges, houseboats, etc. and by industry in railroad cars, warehouses, farm buildings, etc.

For Phase II of the program, 16 custom-built pads were procured from a firm currently engaged in production of the catalytic pads for several of the heater manufacturers. These pads, constructed per the authors' specifications based on the results of earlier testing, are described in detail in Appendix C. Basically, the 16 pads consisted of four groups, each group treated with different catalysts. Each group contained four alumina-silica fiber pads of different thicknesses: 0.95 cm, 1.27 cm, 1.95 cm and 2.54 cm (3/8, 1/2, 3/4 and 1 inch). The first group of pads had been treated with the "standard" platinum loading; the second group had twice the standard loading. Previous fuel additive studies by Martin et al.[13] had shown manganese compounds to be effective in the reduction of one product of incomplete combustion; i.e., carbon particulate. Since the total CO and HC emissions encountered in the additive tests was so low, it was thought

that manganese might have some potential for their reduction when these incomplete combustion products were present in higher amounts. Therefore, the third and fourth groups of the present program had the standard platinum loading plus 0.25 percent and 1.0 percent manganese, respectively.

Standard Fuels

In order to provide uniform test fuels throughout the evaluation, large quantities of two standard fuels were obtained. For the propane heaters, a mixture of Gulf Refinery and Texas Eastern Pipeline--95 percent natural grade (HD5 or better)--was used. The fuel contained only traces of petrolene and butane and was sulfur- and nitrogen-free. For the liquid gas heaters, commercially available Coleman brand liquid fuel was used: it is a refined petroleum naphtha product (high grade gasoline) containing no lead and no halides.

Test Plan

Phase I of the test program was a complete characterization of the 14 commercial heaters and, more specifically, measurement of the fuel consumption rate (heat input) and combustion products of each. All of the heaters were first put through a break-in period of full-out firing for 2 hours, after which they were allowed to cool completely before any testing. Throughout the testing each heater was allowed to warm up for a period of 1 hour before any sampling. Figure 1 is a schematic of the test system used for the LP heaters. The system for the liquid-fired heaters was the same, but each heater utilized its own self-contained fuel supply.

Before the initial test, each heater was permitted to operate full-out under its own control system; i.e., the control valve was wide open on the

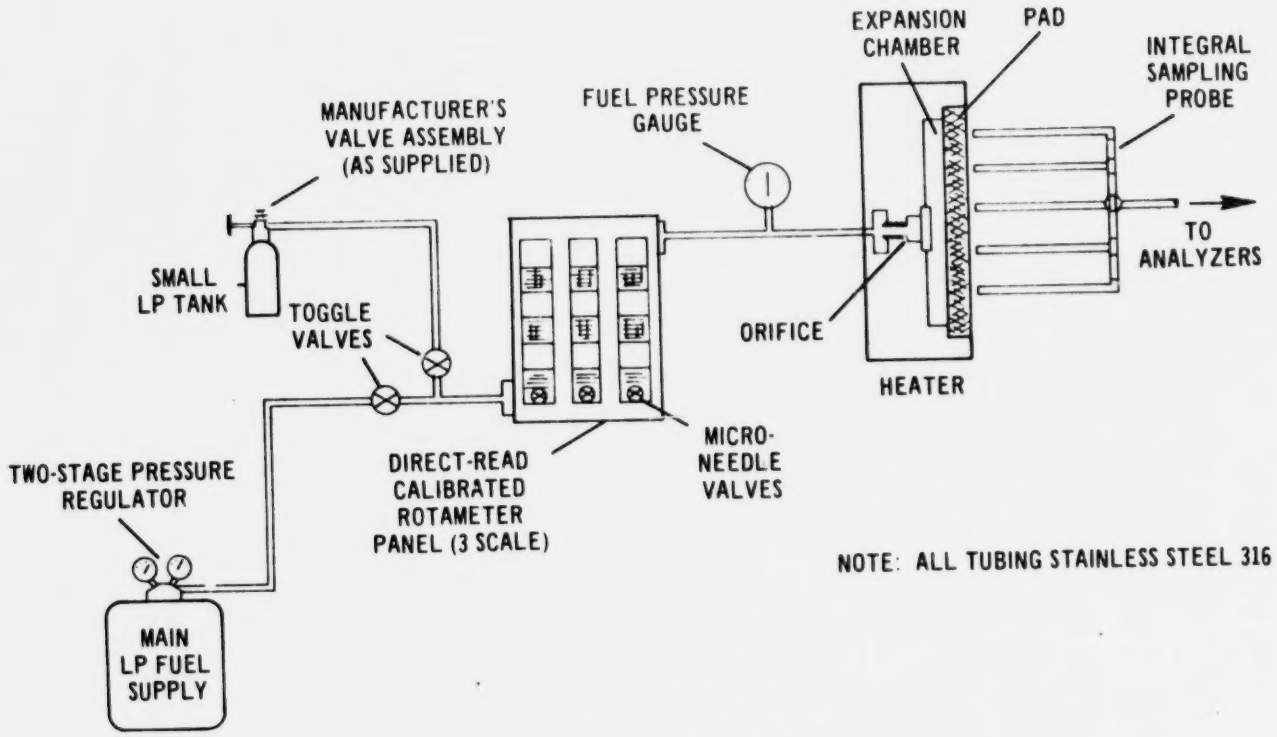


Figure 1. Schematic of test facility.

LP units and the "high" setting was on the liquid fuel ones. During this time the fuel rate and inlet orifice pressure were recorded. In-line pressure gauges and rotameters were used for the propane, while an overall weight loss determination was utilized with the liquid fuel.

Once the operating characteristics of each LP unit had been determined, the fuel supply was switched over to the large tank of standard propane. This switching was necessary to ensure that the results were not affected by pressure variation in the small cylinders of propane normally used with these units. This, of course, was not a problem with the liquid fuel heaters. The first emissions test was run at the "full-out" condition; i.e., the fuel rate from the large tank was adjusted until it matched the rate measured when the heater was "wide open" under the manufacturer's control system. Again, for the liquid-fuel units this "high" setting was used. Continuous emissions measurements were made until the unit reached equilibrium operation.

As a second part of Phase I, all of the heaters were rerun and sampled at a common fuel rate, and therefore a common heat input value (1,008 kcal/hr, 4,000 Btu/hr). This was done in order to have a second, and possibly more valid, basis for comparison. The first test simulated the way the heaters are used in actual practice; the second allowed comparison of the quality of the catalyst pad and fuel delivery system. The common value of (1,008 kcal/hr, 4,000 Btu/hr) was selected because it was in the medium-to-high range of most heaters and yet not far from the maximum value of the least powerful heater. In the case of the liquid fuel models, the heat

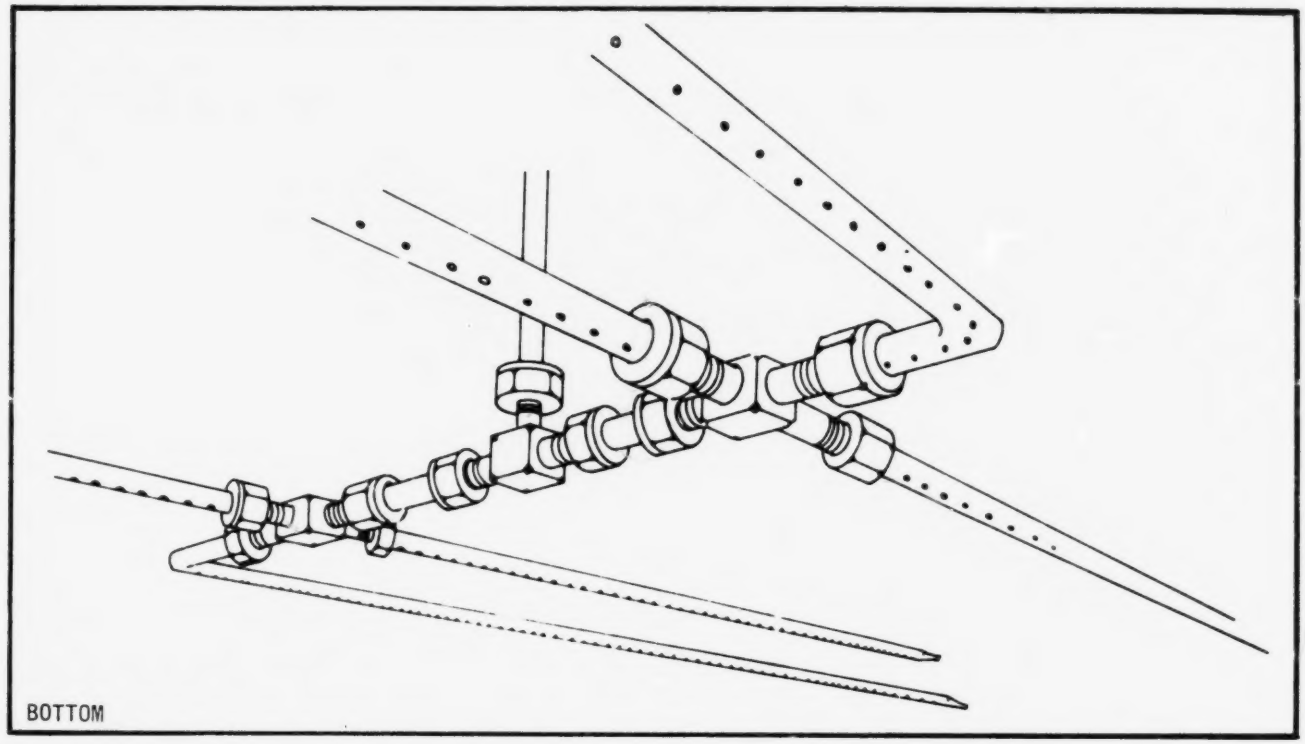
setting (high - medium - low) was adjusted until a value close to (1,008 kcal/hr, 4,000 Btu) was obtained.

For the Phase II testing, each of the 16 custom-built pads was mounted in a conventional propane unit that had been modified to accept the various pad thicknesses. After an initial break-in period of 2 hours, each pad was warmed up for 1 hour and subsequently run and sampled at four different fuel rates in the range of 500 to 850 scc/min (655 to 1108 kcal/hr, 2,600 to 4,400 input Btu/hr).

Probe Design

Since many of the heaters were of different sizes and physical configurations, it was necessary to construct a probe of special design that would incorporate no bias in sampling. A single-point differential probe, while extremely functional for evaluating inhomogeneities characteristic of specific pads, was not satisfactory for a program of this scope. Figure 2 illustrates the first probe which was utilized in the testing. The six prongs welded shut at the ends were made long enough to accommodate the largest heater. Several small holes drilled in the sides of tubes facing the heaters were opened depending upon the size of the pad being tested. In actual practice this probe design was not satisfactory; it was not possible to size the holes correctly to ensure uniform sampling over the wide variety of pads encountered.

Figure 3 shows the probe used to obtain all the results reported herein. The eight prongs of this probe are virtually all of the same length and each has one 90-degree bend before entering the sample line. In addition, by loosening the retaining nuts on the "cross" type fittings and adjusting the prongs, the area covered by the eight points can be greatly reduced or



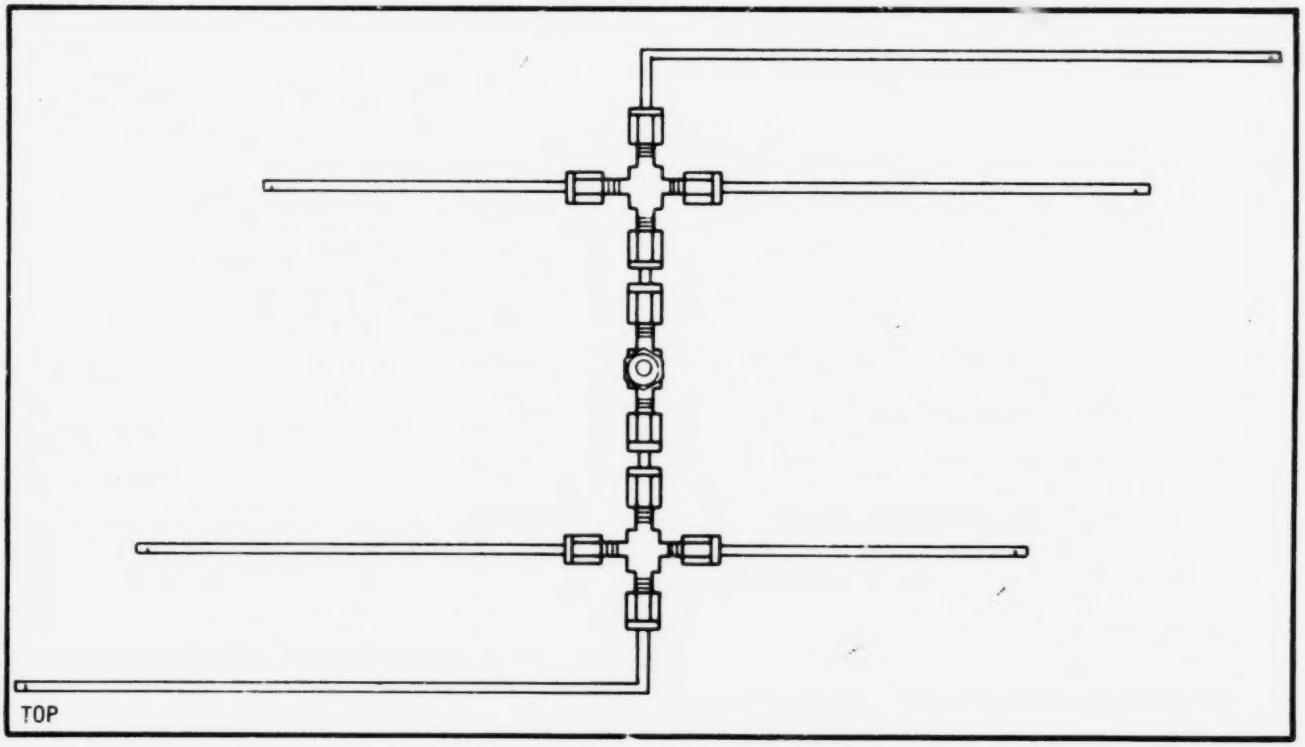


Figure 2. Original probe.

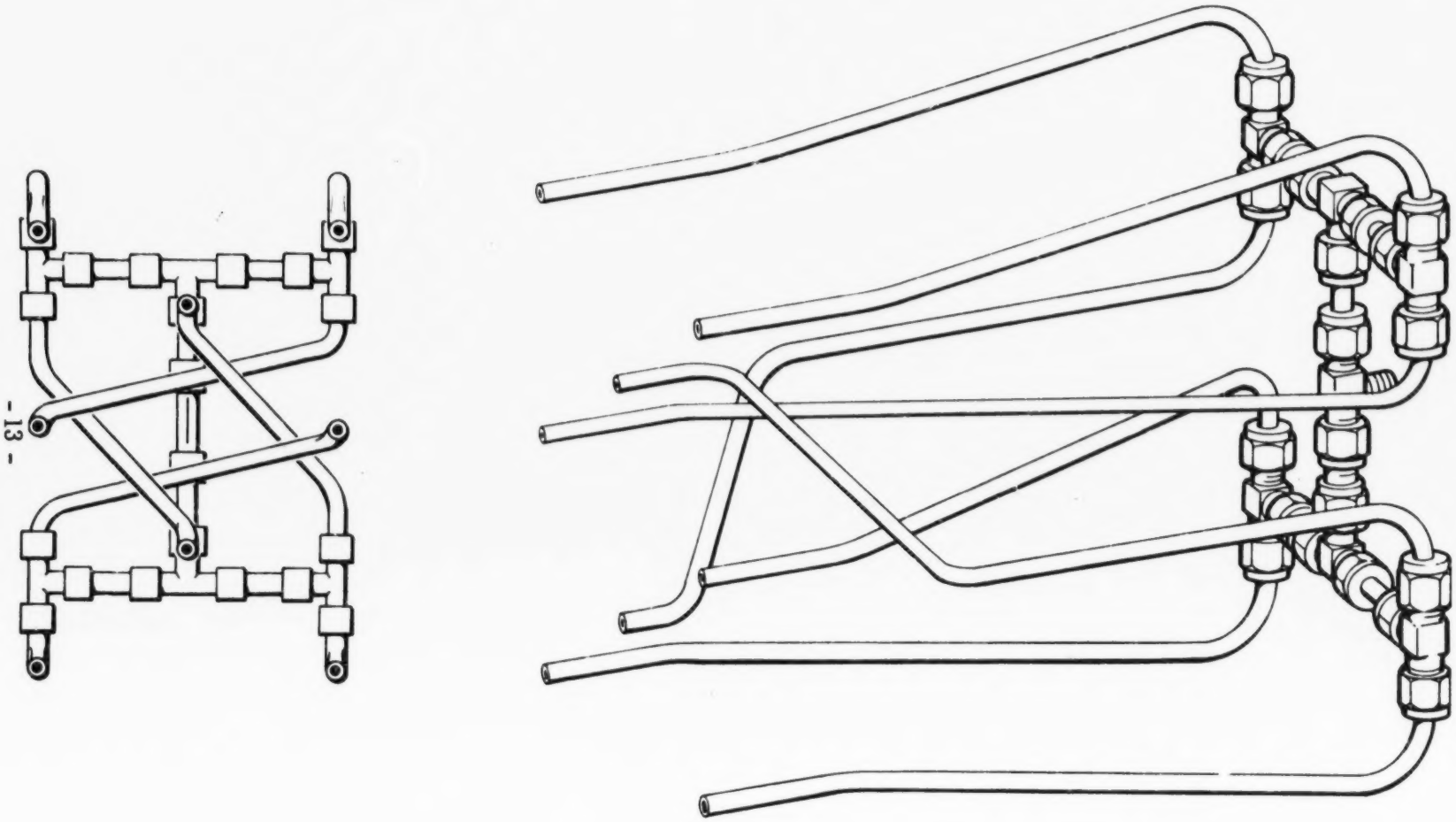


Figure 3. Integral sampling probe.

enlarged without affecting the pressure drop (and therefore the flow rate) of the individual lines. The authors believe this design to be far more uniform in sampling characteristics than any other encountered to date. During sampling, the probe was placed 0.316 cm (1/8-inch) above the pad surface, minimizing dilution of the samples with room air.

Analytical Procedures

With the exception of the probe design just discussed, the sampling and analytical procedures were identical to those employed in earlier studies by the Combustion Research Section: paramagnetic oxygen analysis, flame ionization detection for unburned hydrocarbons, and nondispersive infrared analysis of CO, CO_2, and NO_x. All sampling was done on a continuous basis, and the gaseous hydrocarbons were calculated as propane. Traditional sequential smoke sampling, particulate collection, and SO_2 analysis were omitted due to the negligible ash and sulfur content of the fuels. The details of the entire sampling system are in Appendix D.

ANALYSIS OF RESULTS

Phase I--Commercial Units

Introductory Note: The purpose of this program was to evaluate catalytic combustion as a new concept in residential heating, not to perform a consumer-type evaluation of presently available units. Therefore, the results contained herein may be used neither as a basis for any legal action against any party, nor for sales promotion of any of the products. Also, since most of the testing occurred during the summer of 1971, new models have undoubtedly come on the market. It is hoped, however, that the program will provide insight for future work in the field. In addition, it should be noted that all of the heaters tested were assumed to be representative of their particular brand; however, the possibility that one or more of the units could have been defective should not be ignored.

Table 1 shows a complete listing of each of the commercially available units tested and the emission levels measured at the "full-out" condition. All pollutant concentrations are reduced to zero percent excess air; i.e., air-free. (Appendix E is a detailed explanation of the air-free concept.) As the table indicates, the operating characteristics of the various units were significantly different. CO and unburned HC emissions from the liquid units are considerably higher than from most of the propane units. NO_x emissions are extremely low from nearly all the heaters. Appendix F is a complete listing of all the results, as well as specific comments about each heater.

Table 2 shows both the rated and the measured heating values for the same heaters under "full-out" operation. It is interesting to note that the

Table 1. POLLUTANT EMISSIONS FROM COMMERCIAL UNITS AT MAXIMUM HEAT OUTPUT[a]

Heater	CO[b]	HC[b]	NO_x[b]
LPG MODELS			
Bernzomatic	46	2550	2
Cargo Safe	124	8650	16
Coleman	313	29,000	62
Impala	174	4050	8
McGinnis	20	1000	6
Primus	1560	1[illegible],250	12
Turner (LP7)	27	1110	0
Turner (LP27)	36	1335	4
Zebco	1079	5800	0
White Gas Models			
Coleman (513A-700)	665	7500	8
Coleman (513A-708)	478	8315	Not measured
Coleman (515-700)	2350	19,000	13
Coleman (515A-704)	198	5335	Not measured
Thermos	1280	18,000	32

[a]Fuel control valves set on "high"

[b]Reported as ppm at 0% excess air

Table 2. PERFORMANCE CHARACTERISTICS OF COMMERCIAL UNITS AT MAXIMUM HEAT OUTPUT[a]

Heater	Fuel	Rated Heating Value[b]	Measured Heating Value[b]	Performance Factor[c]
Coleman (515-700)	White Gas	8000	8440	1.06
Cargo Safe	LPG	6000	5970	1.00
Coleman (513A-708)	White Gas	5000	4970	0.99
McGinnis	LPG	8000	7785	0.97
Coleman (513A-700)	White Gas	5000	4750	0.95
Coleman (515A-704)	White Gas	8000	7080	0.89
Primus	LPG	8000	6365	0.80
Impala	LPG	8000	5970	0.75
Thermos	White Gas	7000	4915	0.70
Bernzomatic	LPG	7000	4800	0.69
Turner (LP27)	LPG	7000	4200	0.60
Coleman	LPG	5000	3200	0.64
Zebco	LPG	7000	8330	0.55
Turner (LP7)	LPG	7000	3375	0.48

[a] Fuel control valves set on "high"

[b] Btu/hr based on inlet fuel rate (These values do not include a correction for the fuel lost through the escaping unburned hydrocarbons.)

[c] Measured heating value/rated heating value

ratio of the actual heat output to the manufacturer's rated values range from 0.5 to values slightly in excess of 1.0.

Although all 14 heaters have about the same heat output rating, they vary rather widely in retail cost and in emissions per actual heat unit. Table 3 shows the manufacturer's suggested retail cost of each unit; i.e., the list price. The table also lists a value index and a pollution index. Ideally, the consumer would like to maximize the heat he gets for his dollar and minimize the pollution. Unfortunately, no one heater does both.

It was decided that the experimental data obtained by operating the heaters at an equivalent flow rate of 770 scc/min (1,008 kcal/hr, 4,000 Btu/hr) did not provide a fair basis for comparison. The larger heaters performed very poorly at this reduced rate, probably because it allowed the catalyst pad to cool below the optimum operating temperature, thus confirming the work of other investigators[9].

Table 3. COMPARISON OF COMMERCIALLY AVAILABLE UNITS

Heater	Fuel	Price[a] (Dollars)	Cost/ Effectiveness Index[b]	Pollution Index[c]
McGinnis	LPG	110.00	14.13	3
Turner (LP7)	LPG	45.00	13.33	8
Turner (LP27)	LPG	45.00	10.71	9
Bernzomatic	LPG	45.00	9.38	10
Cargo Safe	LPG	73.00	12.23	21
Coleman (515A-704)	White Gas	64.00	9.04	28
Impala	LPG	50.00	8.38	29
Coleman (513A-708)	White Gas	46.00	9.25	96
Coleman	LPG	47.50	14.85	98
Coleman (513A-700)	White Gas	28.00	5.89	140
Primus	LPG	30.00	4.71	245
Thermos	White Gas	34.00	6.92	260
Coleman (515-700)	White Gas	40.00	4.74	278
Zebco	LPG	40.00	10.44	282

[a] Based on best available information regarding manufacturer's suggested retail price (net cost) in 1971.

[b] Retail cost (dollars)/ 252 x 10^3 cal ($/1000 Btu)

[c] ppm CO (air free)/ 252 x 10^3 cal (ppm/1000 Btu

Phase II--Controlled Testing

The Phase II work was undertaken in an effort to clarify why certain of the commercially available units performed so much better than others. The first step was an analysis of the combustion homogeneity across the pad surface. This was accomplished by taking differential, point-wise emission measurements. The old style Turner (propane) and the Thermos (liquid fuel) were chosen for the tests primarily because each has a grill which makes probe location simple. Figure 4 shows a similar grid pattern with the results of the Turner profiling. Due to time limitations, each grid point was not measured; Figure 4 is based on four carefully selected traverses. The major non-uniformity occurs at the pad edge (see Figure 4) as was expected. The poorer combustion region in the center of the pad is apparently due to the fuel distribution system's blocking the axial flow at this point (see Figure 5). In general, the emissions are reasonably uniform: except for points at the very edge, the standard deviation in the data is less than 83 ppm; approximately 80 percent of the data points are within 10 percent of the sample mean. That fuel distribution problems cannot account for the poor performance of some heaters is a conclusion confirmed by the Thermos profile data.

The major portion of the effort in Phase II was directed toward evaluating the effects of substrate thickness, catalyst type and concentration, and fuel rate on pollutant emissions. Because of the virtually negligible amount of NO_x produced by all the pads, CO and gaseous HC were chosen as the performance parameters to be used for comparison.

Each of the catalyst treatments was examined on substrates of four different thicknesses (0.95, 1.27, 1.95, and 2.54 cm; 3/8, 1/2, 3/4, and 1 inch).

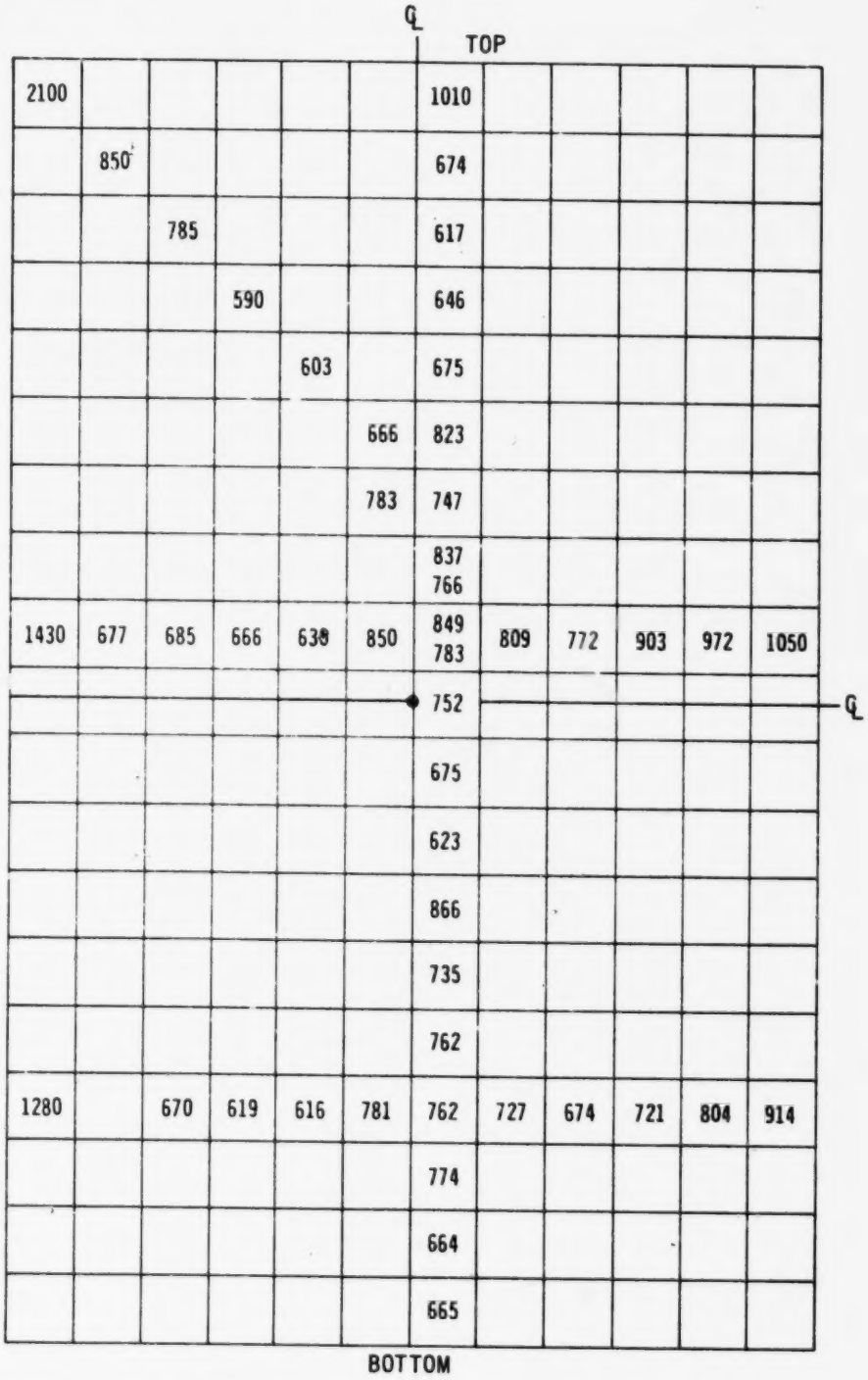


Figure 4. Emission profile (all values are gaseous hydrocarbon in ppm).

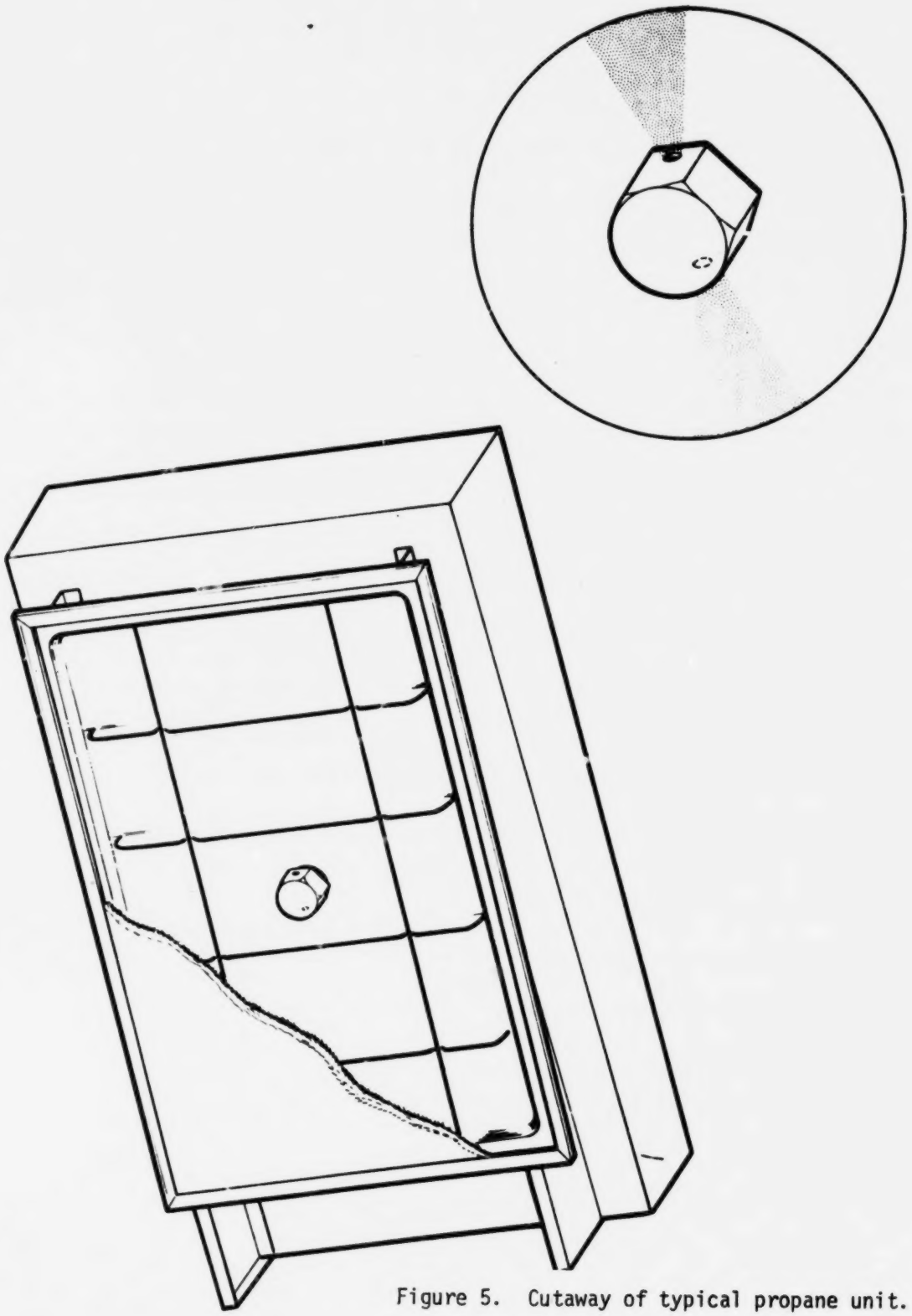


Figure 5. Cutaway of typical propane unit.

Figures 6 and 7 show the effects of substrate thickness variation on HC and CO emissions, respectively, for a sample case. In general, the data from all 16 pads indicate that pad thickness has little, if any, effect.

Figures 8 and 9 show the effects of catalyst composition on HC and CO emissions, respectively. The data on these graphs are the result of averaging the four pad thicknesses with each given catalyst treatment. Figure 8 indicates that doubling the platinum concentration causes a slight but distinct decrease in the HC emissions, especially at the higher fuel rates. Figure 9 suggests that increasing the platinum increases the CO emissions by about 10 ppm. This may be a real effect or it may be an analytical problem due to the extremely low levels of CO.

Figures 8 and 9 also illustrate that under similar operating conditions, the addition of 1.0 percent manganese to the catalyst treatment, while apparently having no effect on CO, did show a slight but distinct decrease in HC emissions. Due to the slight decrease, the 0.25 percent manganese pads were not tested; however, it does appear that further testing at higher concentrations might be in order since manganese is considerably cheaper than platinum.

By far, the most important parameter encountered throughout the entire study was fuel rate, especially with regard to HC emissions (see Figure 8). Indeed, every pad tested produced a parabolic emission curve; interestingly enough, the minimum vertices of the curves fall consistently in the 625-675 scc/min range. Further, a fuel rate variation in either direction of as little as 150 scc/min results in a two- to three-fold increase in unburned HC emissions. The effect was not as pronounced for CO emissions; however,

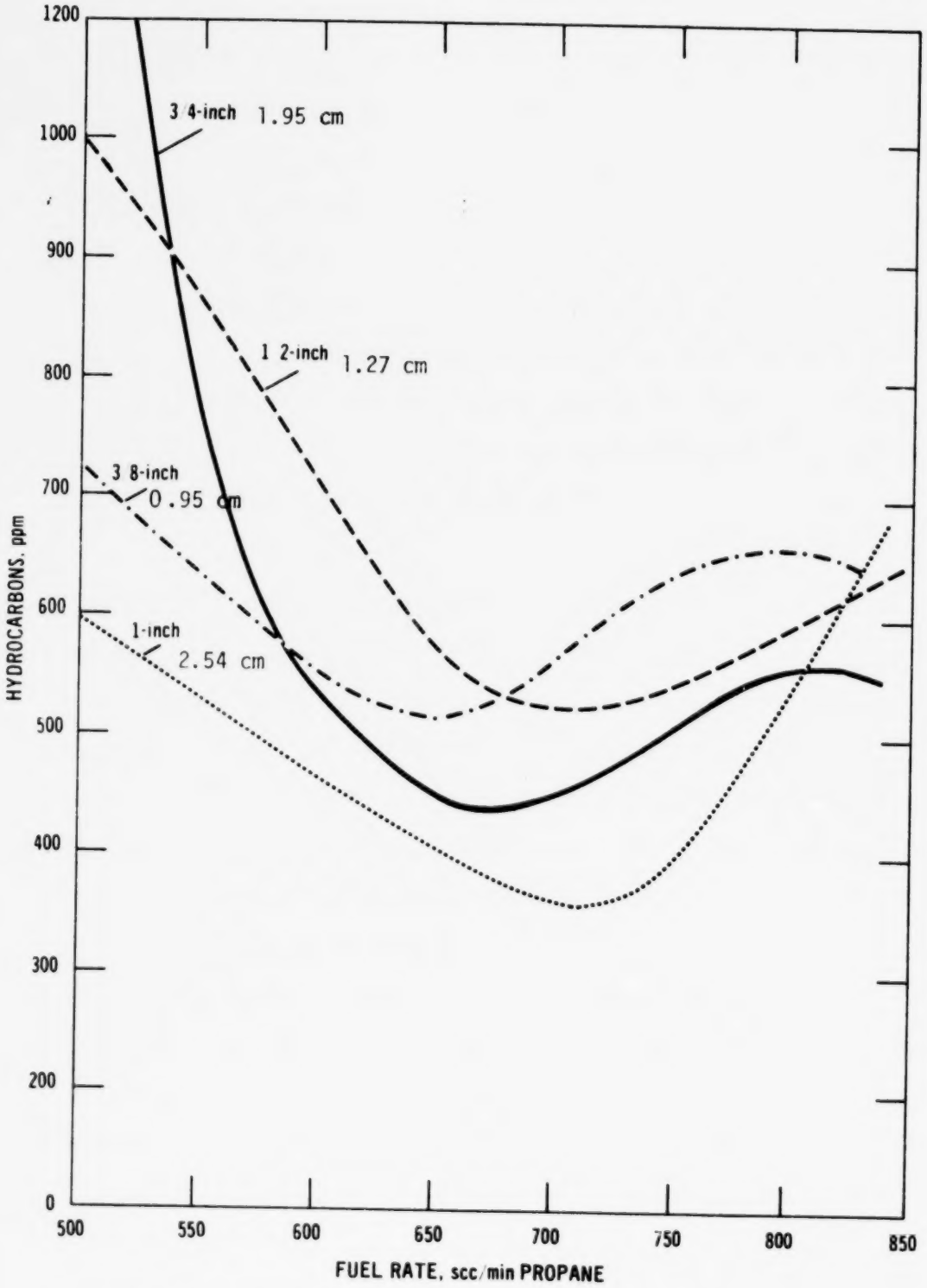


Figure 6. Typical case of hydrocarbon emissions for different pad thicknesses.

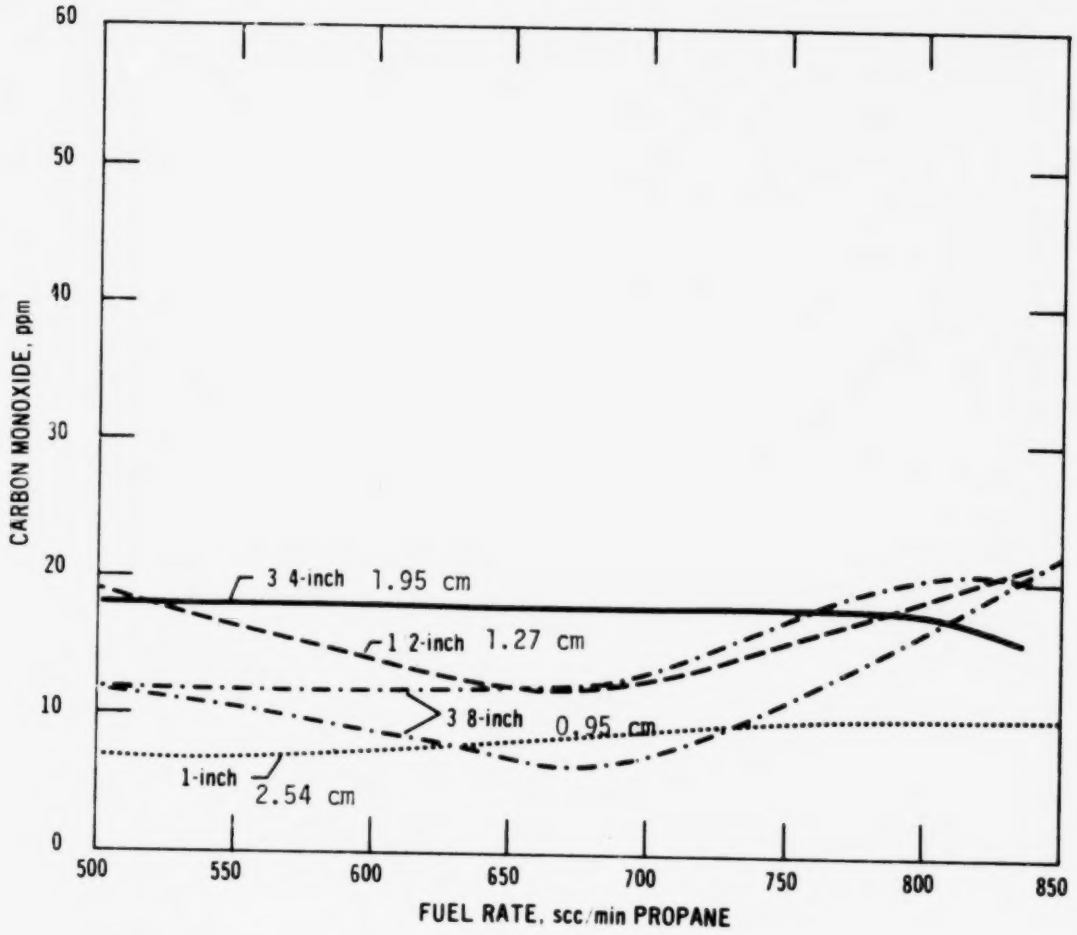


Figure 7. Typical case of carbon monoxide emissions for different pad thicknesses.

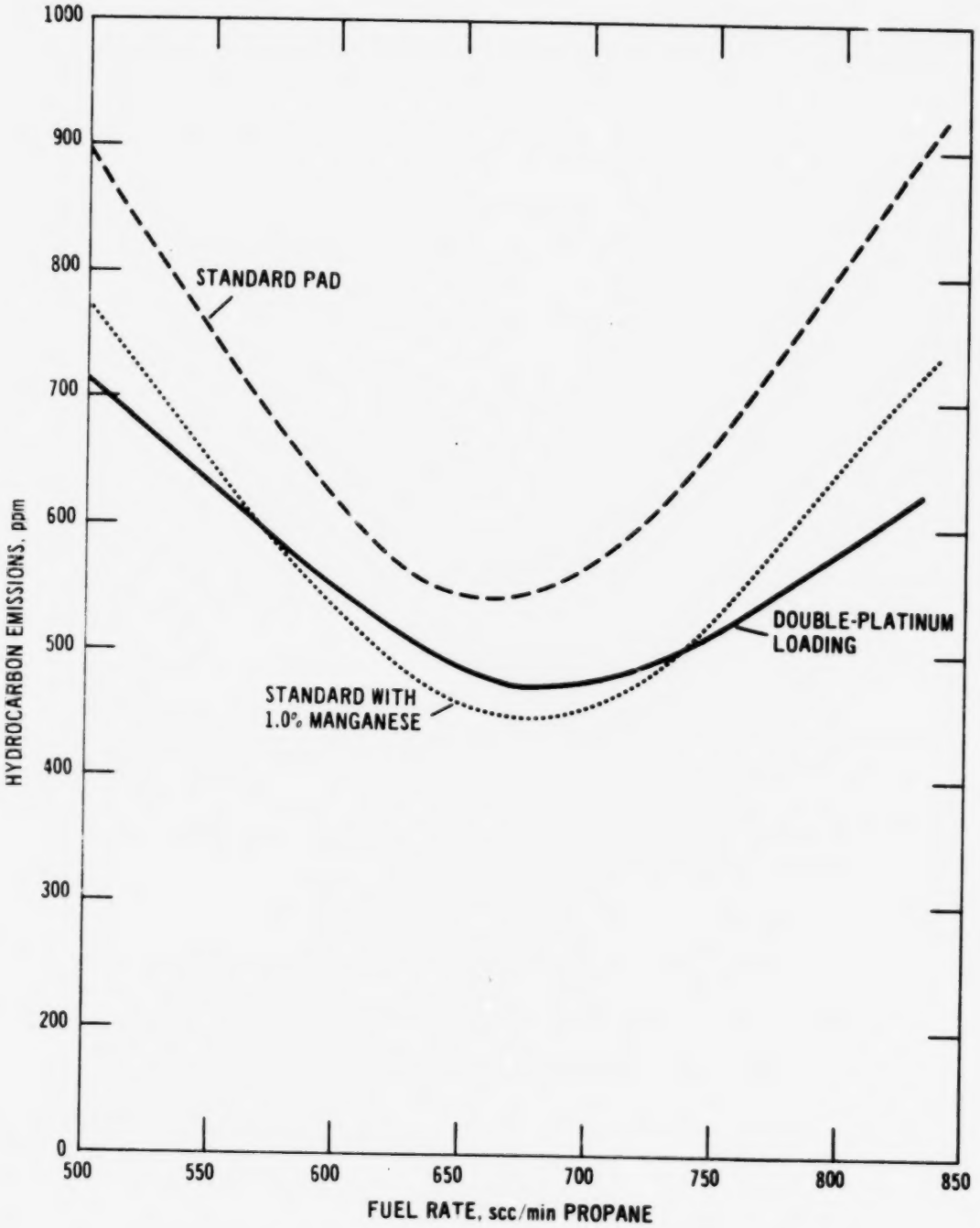


Figure 8. Comparison of pad types versus hydrocarbon emissions.

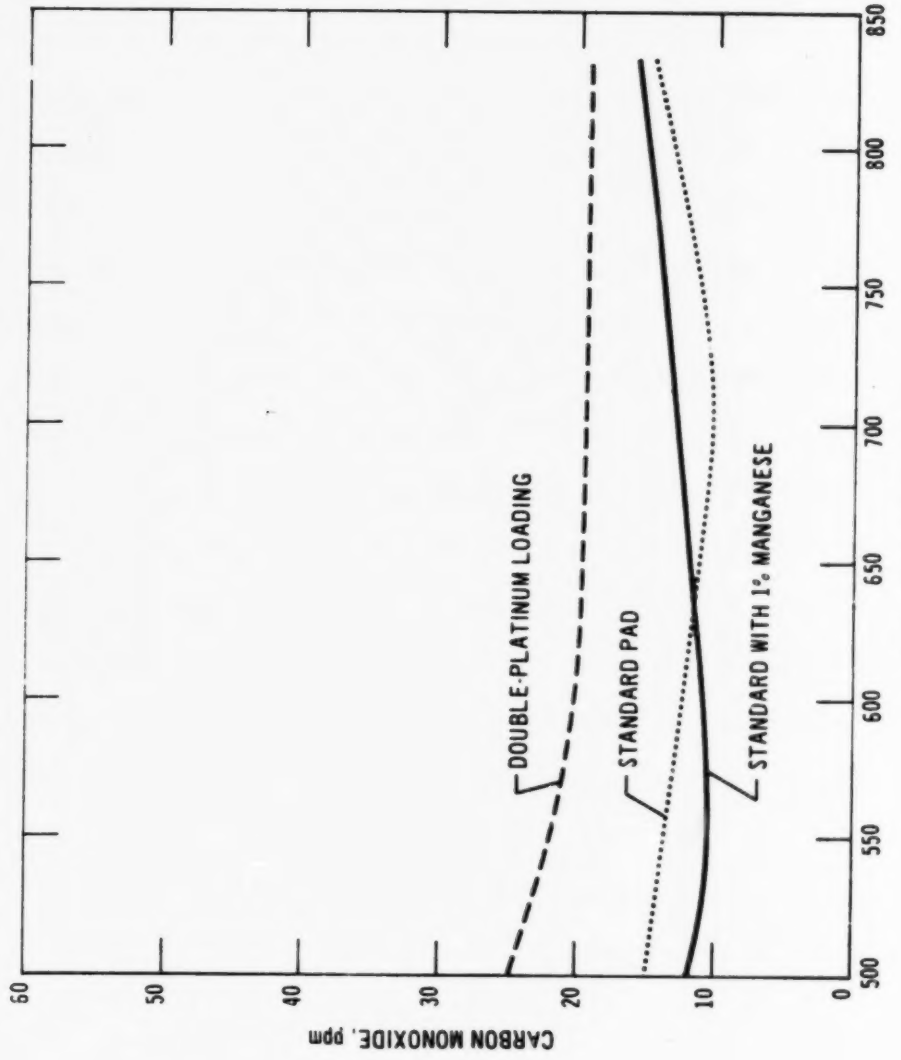


Figure 9. Comparison of pad types versus carbon monoxide emissions.

the reader should keep in mind that the CO levels from all the pads were extremely low compared to many of the commercial heaters.

The parabolic nature of the curve is probably due to competition between pad temperature and mass transfer effects. If the fuel rate is too low, the pad fails to achieve and sustain the temperatures needed for efficient catalyst performance.

On the other hand, as the flow rate is increased beyond a certain point, temperature effects become small and the reaction becomes mass-transfer-limited, specifically by the rate of diffusion of oxygen to the catalytic surface From the catalyst geometry, fuel flow, and temperature of each unit it was possible to compute diffusional rates of oxygen to the surface of the pad. Using these with the measured fuel rate data, air-fuel ratios at the surface were then calculated[14]. The results of these calculations for both the commercial units and the custom pads are shown in Figures 10 and 11. In general, the high emission cases are at conditions computed as fuel rich; i.e.,where the superficial propane velocity through the pad exceeds the rate at which stoichiometric amounts of oxygen can diffuse to the pad surface. Quantitatively, this appears to occur when the superficial propane velocity through the pad exceeds about 0.0244 cm/sec (0.0008 ft/sec).

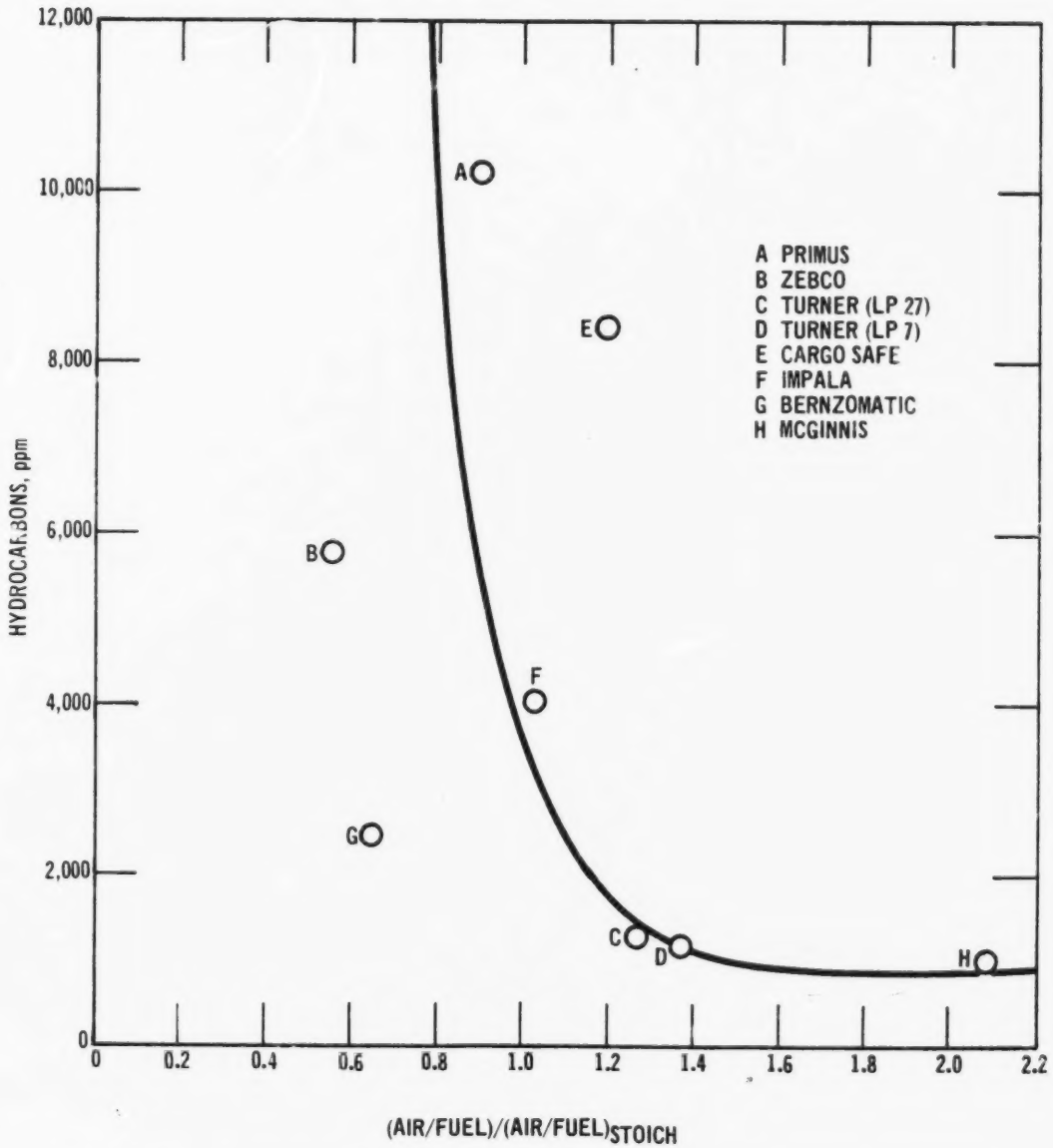


Figure 10. Hydrocarbon emissions versus surface stoichiometric ratio (propane).

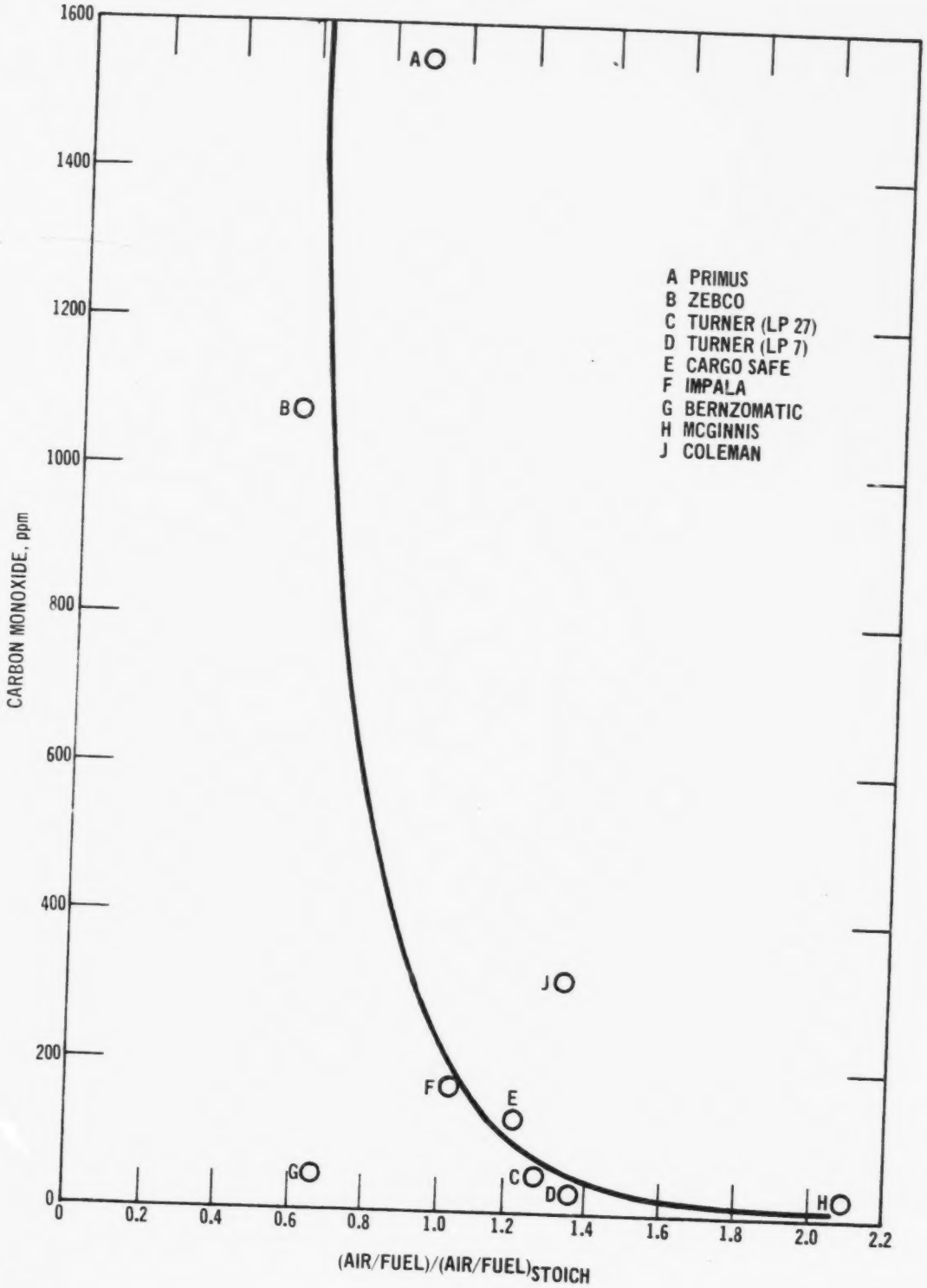


Figure 11. Carbon monoxide emissions versus surface stoichiometric ratio.

Toxicology

Before any final conclusions can be formulated it is necessary to consider the relative importance of the resultant emissions. In general, such aliphatic HC emissions as propane are biologically and chemically inert; i.e., they produce no detectable functional or subclinical alternaticns.[15] Available evidence indicates that these gases are rapidly eliminated from the lungs in an unchanged state. Thus propane gas can be tolerated in relatively high concentrations in inspired air without producing systemic effects.[15] If the concentration is high enough to dilute or exclude the oxygen normally present in air, the effects produced will be due strictly to oxygen deprivation or asphyxia. For instance, a concentration of 100,000 ppm (10 percent), though not noticeably irritating to eyes, nose, or respiratory tract, will produce dizziness within a matter of minutes. But more realistically, exposures to 10,000 ppm (1 percent) cause no symptoms in man. Even odor is not detectable below 20,000 ppm (2 percent).[16]

Only one of the LPG heaters tested produced enough gaseous HC to warrant consideration relative to HC toxicity presuming a continuous supply of fresh air is provided. One Coleman unit produced 29,000 ppm; the others ranged from 1,000 to 10,000 ppm. Of the units burning white gasoline, both the Coleman 515-700 and the Thermos produced greater than 10,000 ppm. CO is a specific chemical asphyxiant which combines with the hemoglobin in the blood to exclude oxygen.[9] The U. S. standard for gas-fired room heaters[17] states, "A room heater shall produce no carbon monoxide. This provision shall be deemed met when a concentration of carbon monoxide not in excess of 0.02 percent (200 ppm) is present in an air-free sample of the products of

combustion, when the heater is tested in a room with approximately a normal oxygen supply." All of the liquid fuel units and at least two of the LP heaters operating at maximum heat output produced CO close to or in excess of this limit; in some cases as much as two orders of magnitude higher. On the other hand, four of the units averaged less than 50 ppm, suggesting that high emissions are not necessary. (The authors realize that the units tested are not strictly "room heaters" as such, but the normal applications (e.g., tents, campers, boats, and garages) put them in virtually the same category.)

Domestic Applications

The value of the catalytic combustion concept is that it operates at a low temperature, which considerably limits the formation of NO and the chance of fire. In addition, a few of the commercial units and the work of Phase II have shown that it is possible to operate at relatively low CO and NO levels. Table 4 compares the catalytic heating emissions measured in Phase II with those reported previously[3] for a typical home oil burner. Although the two are not directly comparable for many reasons, they show that the HC emissions from catalytic units are several orders of magnitude greater than from units now being used. Since these emissions considerably enhance the formation of photochemical smog, catalytic heating cannot even be considered as a viable domestic heating alternative until this problem is overcome. Note that this conclusion does not apply to sportsman-type uses because of the relatively small number of units of that type in operation.

Table 4. COMPARISON OF CATALYTIC HEATING EMISSIONS WITH A DOMESTIC OIL BURNER

Emission	Catalytic Combustion[a]	Classical Combustion[a]
CO	0.36	0.40
NO_x	<0.04	0.72
HC	14.0	0.05

[a] gms of pollutant per kg of fuel burned

CONCLUSIONS

1. Commercially available catalytic combustion units vary widely in both actual heat output (for the same rated value) and in pollutant emissions produced. At least four of the heaters examined produced CO levels which are not acceptable and, compared to other units of comparable price, not necessary.
2. Controlled tests reveal that fuel rate is the most critical variable for a given pad size. Pad thickness and platinum concentration have lesser effects on performance.
3. By optimizing the pad thickness, catalyst treatment, and fuel rate it is possible to limit CO emissions to a level approaching that currently possible with conventional domestic heating units. In addition, NO_x formation is essentially zero.
4. For domestic applications the biggest obstacle from the pollution standpoint is that of excessive HC emissions. Further work must be done in this area if the concept is to receive widespread usage.

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RECOMMENDATIONS

1. Before any further consideration is given to use of catalytic heating for domestic applications, it must be shown that present hydrocarbon levels can be substantially reduced.
2. Manufacturers' warnings regarding ventilation requirements should be strengthened.
3. Manufacturers should make a concentrated effort to improve performance because data shows that some units operate much better than other units of equivalent price.
4. Safety standards for catalytic heaters are needed to protect the public from the health hazards of inferior quality units.

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Appendix A. LIST OF COMMERCIAL CATALYTIC HEATERS USED IN TEST PROGRAM

Brand	Model	Heat rating, Cal (Btu)	Pad configuration	Retail cost, $
LPG Fired				
Bernzomatic	TX950	$252x10^3$ - $1764x10^3$ (1000 - 7000)	19.05 cm diameter (round)	44.95
Cargo Safe	----	$1512x10^3$ cal/g (6000)	25.08x29.8 cm vertical rectangle	73.20
Impala	Master-Port 8000-36-LP	$2016x10^3$ (8000)	22.8x28.6 cm vertical rectangle	50.00
McGinnis	C4G Gas Pre-Heat	$2016x10^3$ (8000)	53.3x27.3 cm horizontal rectangle	110.00
Primus	Duo-Flow 8	$504x10^3$-$2016x10^3$ (2000 - 8000)	36.8x14 cm angled double-face horizontal rectangle	29.99
Turner (LP7)	LP7	$1764x10^3$ (7000)	18x26.7 cm vertical rectangle	44.95
Turner (LP27)	LP27	$1764x10^3$ (7000)	26.7x18 cm horizontal rectangle	44.95
Zebco	Traveler 7000	$504x10^3$x$1764x10^3$ (2000 - 7000)	27.3x17.8 cm horizontal rectangle	39.95
Coleman	5445-708	$504x10^3$-$1260x10^3$ (2000 - 5000)	26.7x16.5 cm vertical rectangle	47.50

Appendix A (Continued). LIST OF COMMERCIAL CATALYTIC HEATERS USED IN TEST PROGRAM

Brand	Model	Heat rating, Cal (Btu)	Pad configuration	Retail cost, $
Liquid Fired				
Coleman (515-700)	515-700 Dial Temp. Adj.	1260×10^3-2016×10^3 (5000 - 8000)	26.7 cm diameter hemisphere	39.98
Coleman (513A-700	513A-700 Dial Temp. Adj.	756×10^3-1260×10^3 (3000 - 5000)	18.4 cm diameter hemisphere	27.98
Thermos	8512	1764×10^3 (7000)	19.5 cm diameter hemisphere	34.00
Coleman (513A-708)	512A-708	756×10^3-1260×10^3 (3000 - 5000)	18.4 cm diameter hemisphere	45.95
Coleman (515A-704)	515A-704	$1260 \times 10^3 \times 2016 \times 10^3$ (5000 - 8000)	26.7 cm diameter hemisphere	63.95

Appendix B. LIST OF MANUFACTURERS OF CATALYTIC HEATERS USED IN TEST PROGRAM

Bernzomatic
740 Driving Place
Rochester, New York 14613

Phone: 716/458-7076

Cargo Safe
9918 Atlantic Avenue
South Gate, California 90280

Phone: 213/564-2733

Coleman Company, Inc.
250 North Street Francis Avenue
Wichita, Kansas 67201

Phone: 316/267-3211

Impala Industries
1106 East 37th Street
Wichita, Kansas 67204

Phone: 316/838-1486

King Seely Thermos Company
Thermos Division
Norwich, Connecticut 06360

Phone: 203/887-1671

McGinnis Marine, Inc.
5320 28th Street, N.W.
Seattle, Washington 98107

Phone: 206/782-5777

Primus-Sievert
354 Sackett Point Road
New Haven, Connecticut 06473

Phone: 203/239-2554

Turner Corporation
821 Park Avenue
Sycamore, Illinois 60178

Phone: 815/895-4545

Zebco-Brunswick Corporation
P. O. Box 270
Tulsa, Oklahoma 74101

Phone: 918/836-5581

Appendix C. DESCRIPTION OF CUSTOM CATALYTIC PADS

1. Standard Cataheat "P" cover top surface.
2. Standard Cataheat "P" with twice platinum loading cover top surface only.
3. Standard pad and platinum loading with 0.25 percent manganese in excess top surface covering.
4. Standard pad and platinum loading with 1.0 percent manganese in excess top surface loading.

All pads were 18 cm (7-1/8 inches) wide x 26.7 cm (10-1/2 inches) high and were mounted vertically.

Appendix D. SAMPLING SYSTEM AND INSTRUMENTATION

Automatic instrumentation was used to continuously record the concentrations of CO_2, O_2, CO, NO_x and gaseous HC in the exhaust gases, as described below:

Parameter	Instrument Brand & Model	Type
CO_2	Beckman 315 A	Non-dispersive infrared
O_2	Beckman F3M3	Paramagnetic
CO	Beckman 315 A	Non-dispersive infrared (with CO_2 filter)
NO_x	Beckman 315 A1	Non-dispersive infrared
HC	Beckman 400	Flame ionization (calibrated as propane)

All sampling was done at a rate of 1 liter per minute. The sample lines were all constructed of 635 cm I.D. 316 stainless steel tubing except for the NO_x NDIR where 635 cm I.D. Teflon tubing was used (see Figure D-1).

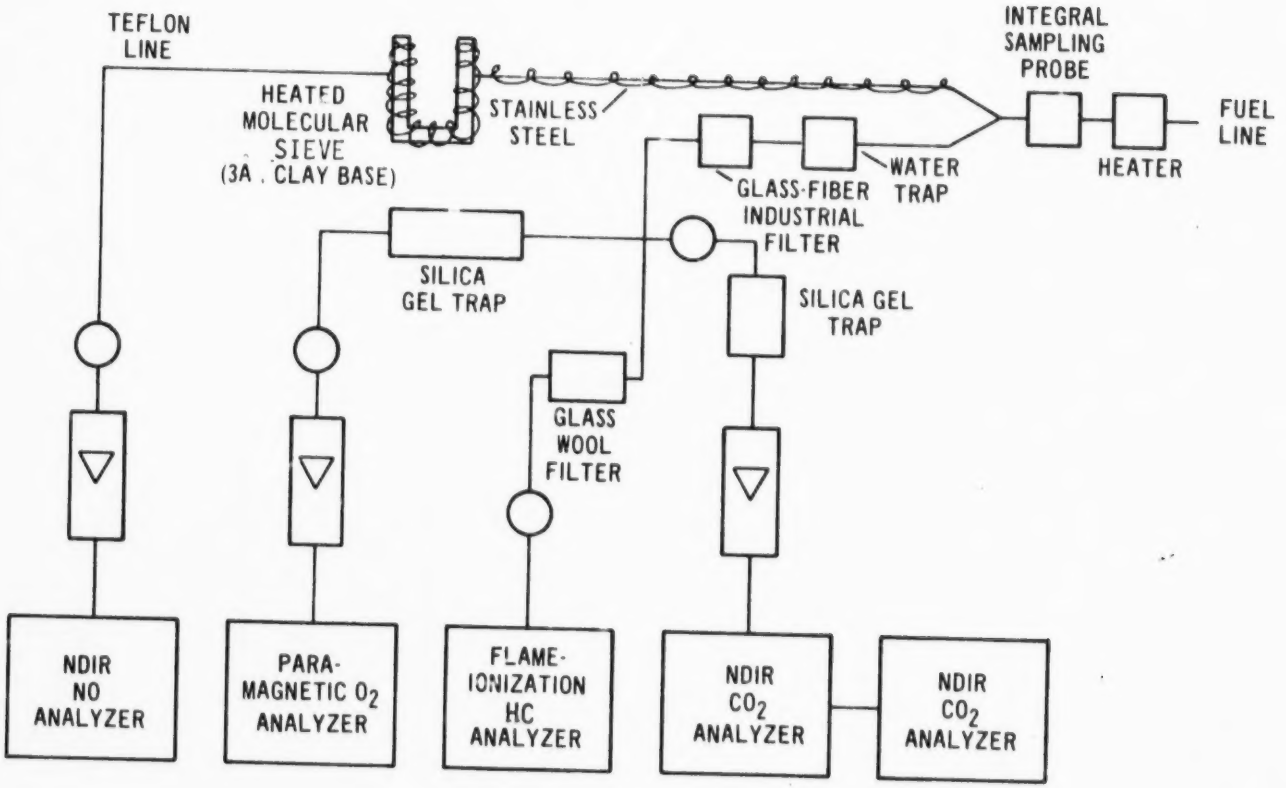

Figure D-1. Analytical system.

Appendix E. EXPLANATION OF AIR-FREE CONCEPT

Based on the composition of fuel burned, it is possible from stoichiometry to calculate the quantity of CO_2 produced by burning a given mass of that fuel. At the conditions in which the volume of air consumed is exactly the same as the amount necessary for complete combustion of the fuel (i.e., stoichiometric), the O_2 concentration in the flue gas is zero. With any excess air, the CO_2 concentration is decreased, and the O_2 concentration is increased, by dilution with air. From the CO_2 and O_2 concentrations, it is possible to calculate the actual volume of flue gas produced. For pollutants (NO, CO, etc.) the concentrations can be normalized to a basis of comparison independent of excess air by multiplying the measured concentration by the ratio of actual volume of flue gas to the volume of flue gas at stoichiometric conditions. In this manner, the pollutant emissions from a device operating at various excess airs can be compared on a common basis, termed "air-free."

Appendix F. SPECIFIC RESULTS AND COMMENTS

Heater	Sample configuration[a]	Kcal/Hr (Btu/hr[b])	CO[c]	HC[c]	NO_x[c]	Heat rate basis
Bernzomatic	Entire face	1209 (4800)	46	2550	2	Natural draw
	Entire face	1007 (4000)	6	2670	12	1007 cal kg/hr
	L/R average	1675 (6650)	46	355	1	(4000 Btu/hr)
Cargo Safe	Bottom 1/2	1504 (5970)	115	5400	14	Natural draw
	Top 1/2	1504 (5970)	133	11900	20	
	Bottom 1/2	1007 (4000)	16	550	7	
	Top 1/2	1007 (4000)	22	440	7	1007 cal kg/hr (4000 Btu/hr)
Impala	Bottom 1/2	1504 (5970)	65	1350	6	
	Top 1/3	1504 (5970)	290	6300	10	Natural draw
	Bottom 1/2	1007 (4000)	60	28000	7	
	Top 1/2	1007 (4000)	125	15000	2	1007 cal kg/hr (4000 Btu/hr)
McGinnis	L/M/R average	1961 (7785)	20	1000	6	Natural draw HIGH
	Average on "LOW"	1915 (7600)	22	1500	3	Natural draw LOW
Primus	L/R average	1603 (6365)	1560	10260	12	Natural draw
	L/R average	1007 (4000)	1280	3000+	7	1007 cal kg/hr (4000 Btu/hr)
Turner (LP7)	T/B average	850 (3375)	27	1100	0	Natural draw
	Entire face	1007 (4000)	12	340	4	1007 cal kg/hr (4000 Btu/hr)

Appendix F (Continued). SPECIFIC RESULTS AND COMMENTS

Heater	Sample configuration[a]	Kcal/Hr (Btu/hr[b])	CO[c]	HC[c]	NO_x[c]	Heat rate basis
Turner (LP27)	Entire face	1058 (4200)	36	1335	2	Natural draw
	Entire face	1007 (4000)	12	688	4	1007 Cal kg/hr (4000 Btu/hr)
Zebco	Entire face	965 (3830)	1079	5800	Not measured	Natural draw
Coleman (515-700)	Entire face on HIGH	2126 (8440)	2300	2000+	13	Natural draw
	Entire face on HIGH	2126 (8440)	2400	1700+	52	Same but with probe raised
Coleman (513A-700)	Entire face on HIGH	1197 (4750)	665	7500	8	Natural draw
	Entire face on LOW	873 (3465)	80	995	6	Natural draw
Coleman (513A-708)	Entire face on HIGH	1252 (4970)	478	8315	Not measured	Natural draw
Coleman (515A-704)	Entire face on HIGH	1783 (7080)	198	5335	Not measured	Natural draw
Coleman (LPG)	Entire face on HIGH	806 (3200)	313	29000	Not measured	Natural draw
Thermos	Entire face	1238 (4915)	1280	18000	32	Natural draw (no control)

[a] L/R - average of left half and right
L/M/R - average of left third, middle third, and right third
T/B - average of top half and bottom half

[b] Calculated values based on fuel rate

[c] Reported as ppm air-free